Clx to Cly Recovery: New Insights from SOLVE Observations of ClO, ClOOCl, and $ClONO_2$

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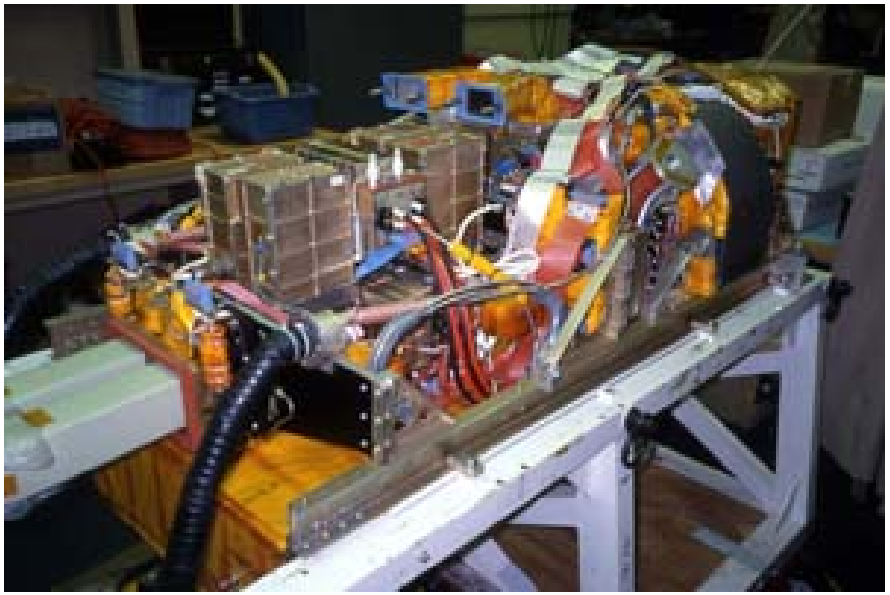


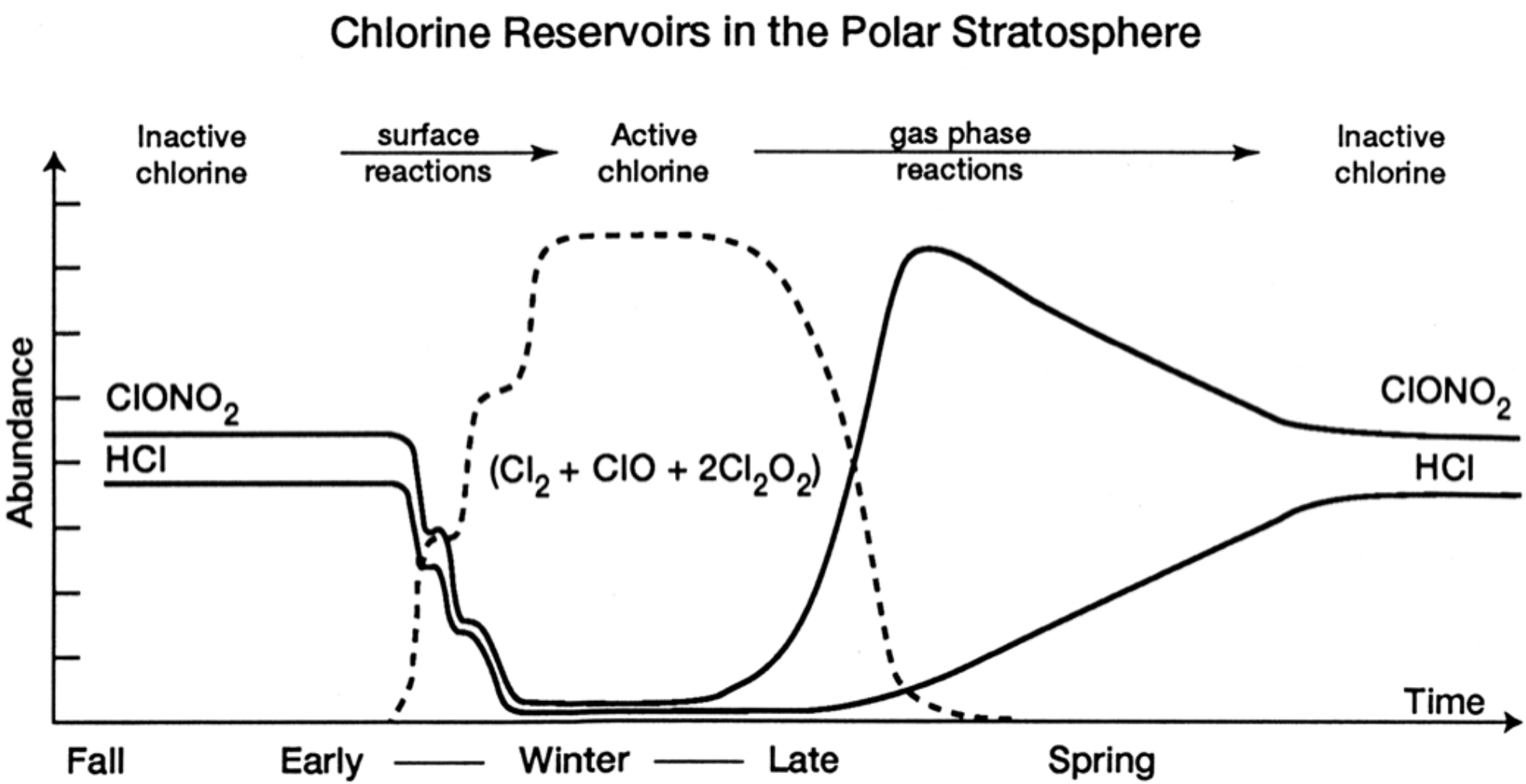
Clx to Cly Recovery during SOLVE

A quantitative understanding, based upon in situ observations, concerning how the chemical activated vortex (Clx/Cly ~ 1) recovers to normal levels (Clx/Cly~ .03) has not been achieved.

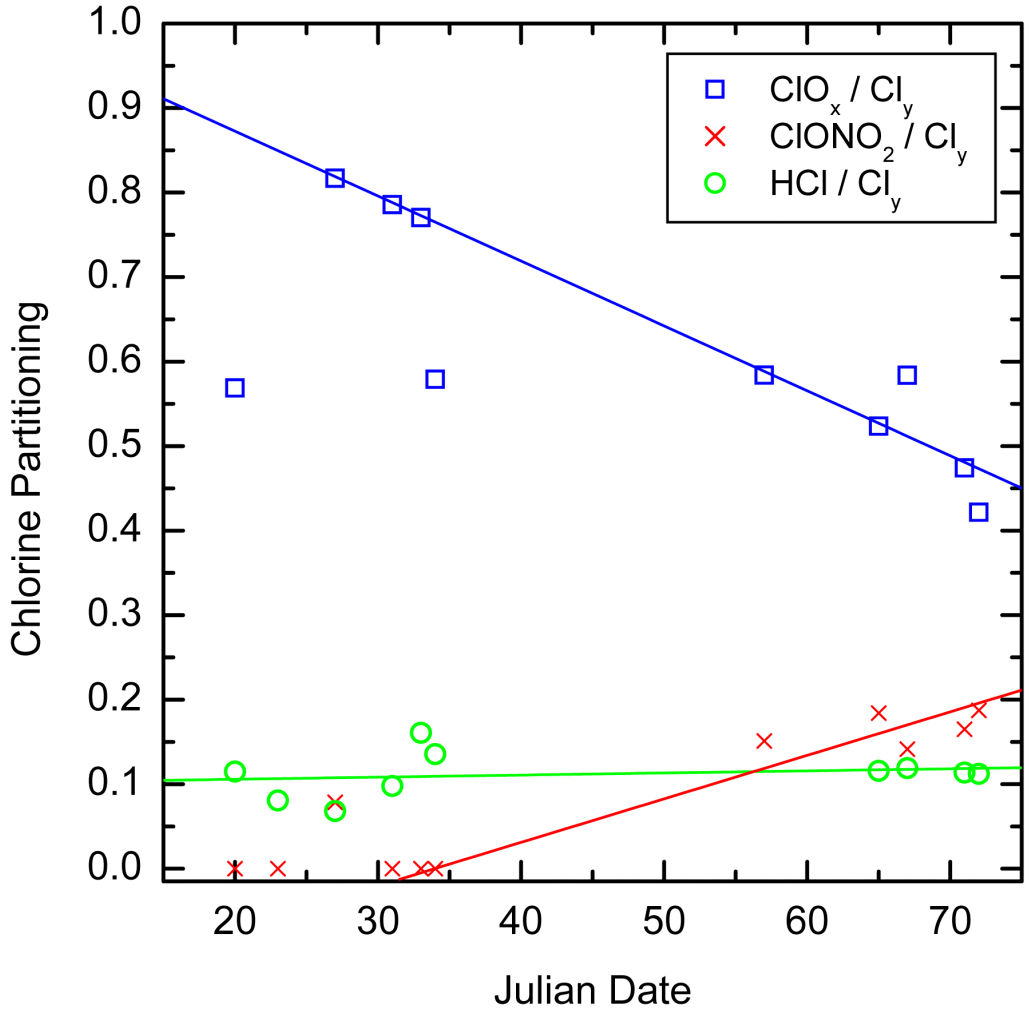
An earlier analyses (1994), based upon HCl observations in the absence ClONO2 observations, suggested recovery of high Clx preferentially into ClONO2, compared to HCl (in the Arctic).

Our SOLVE observations of ClO, ClOOCl and ClONO2 contradict this view. We do not see enough ClONO2 in the late Feb to Mar time frame to support this notion.

From the WMO Report 1994:

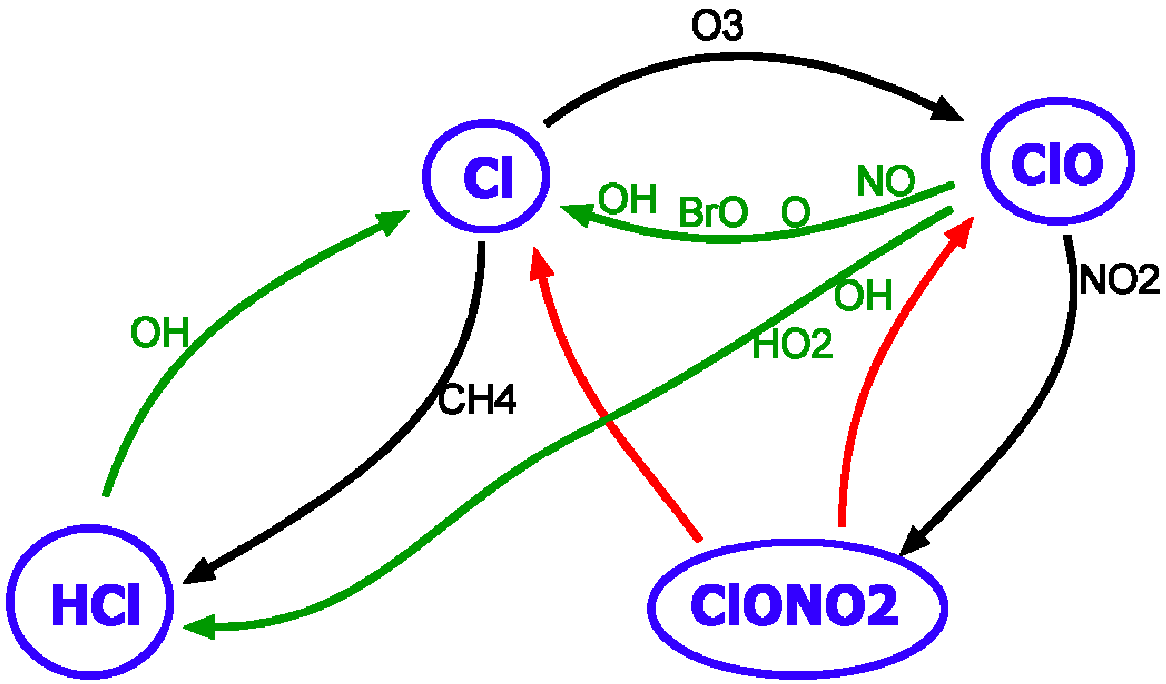


SOLVE Results

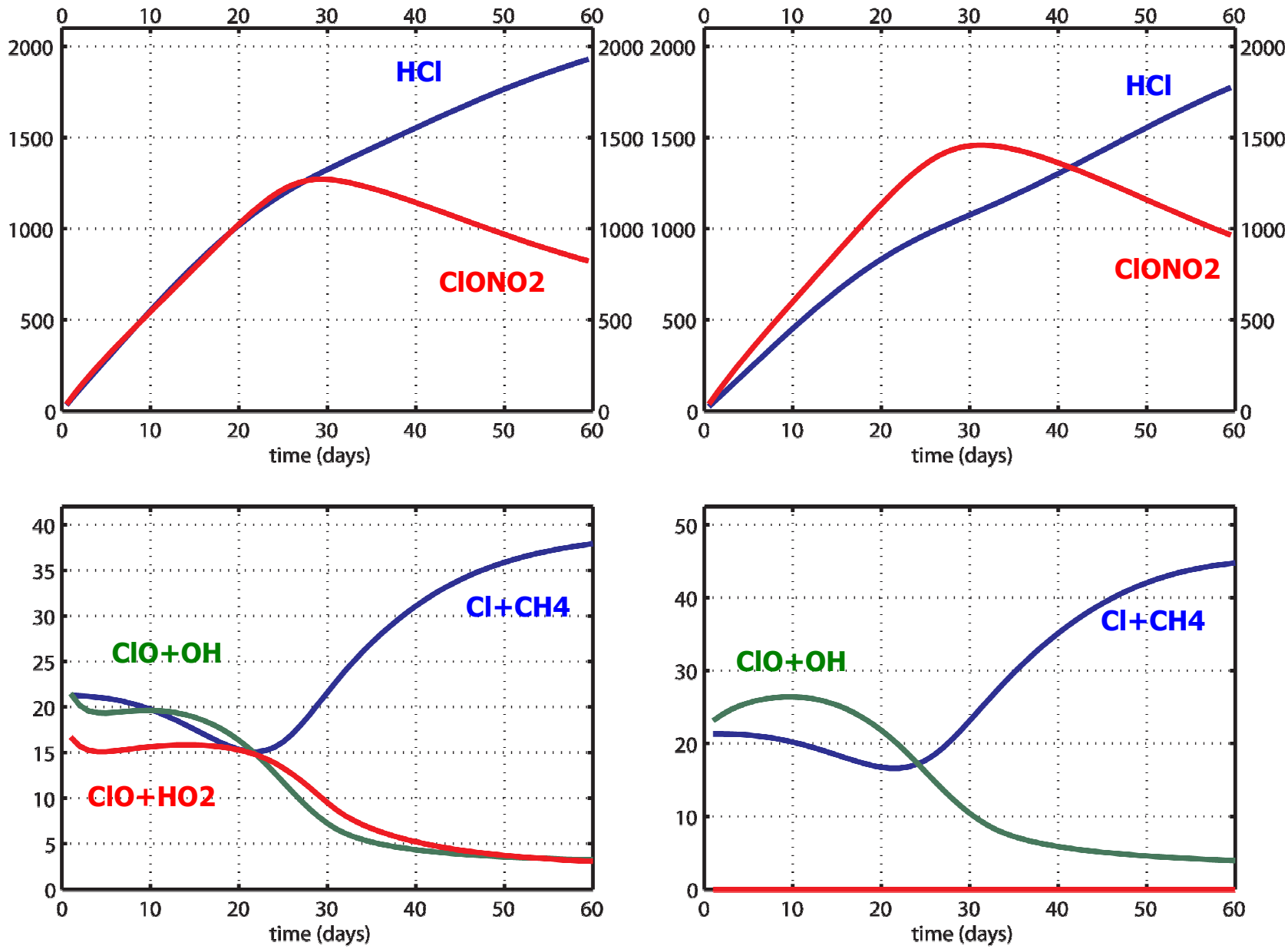


	Late Jan	Early Mar
Clx	80%	50%
ClONO2	0%	18%
HCl	10%	11%
Total	90%	79%

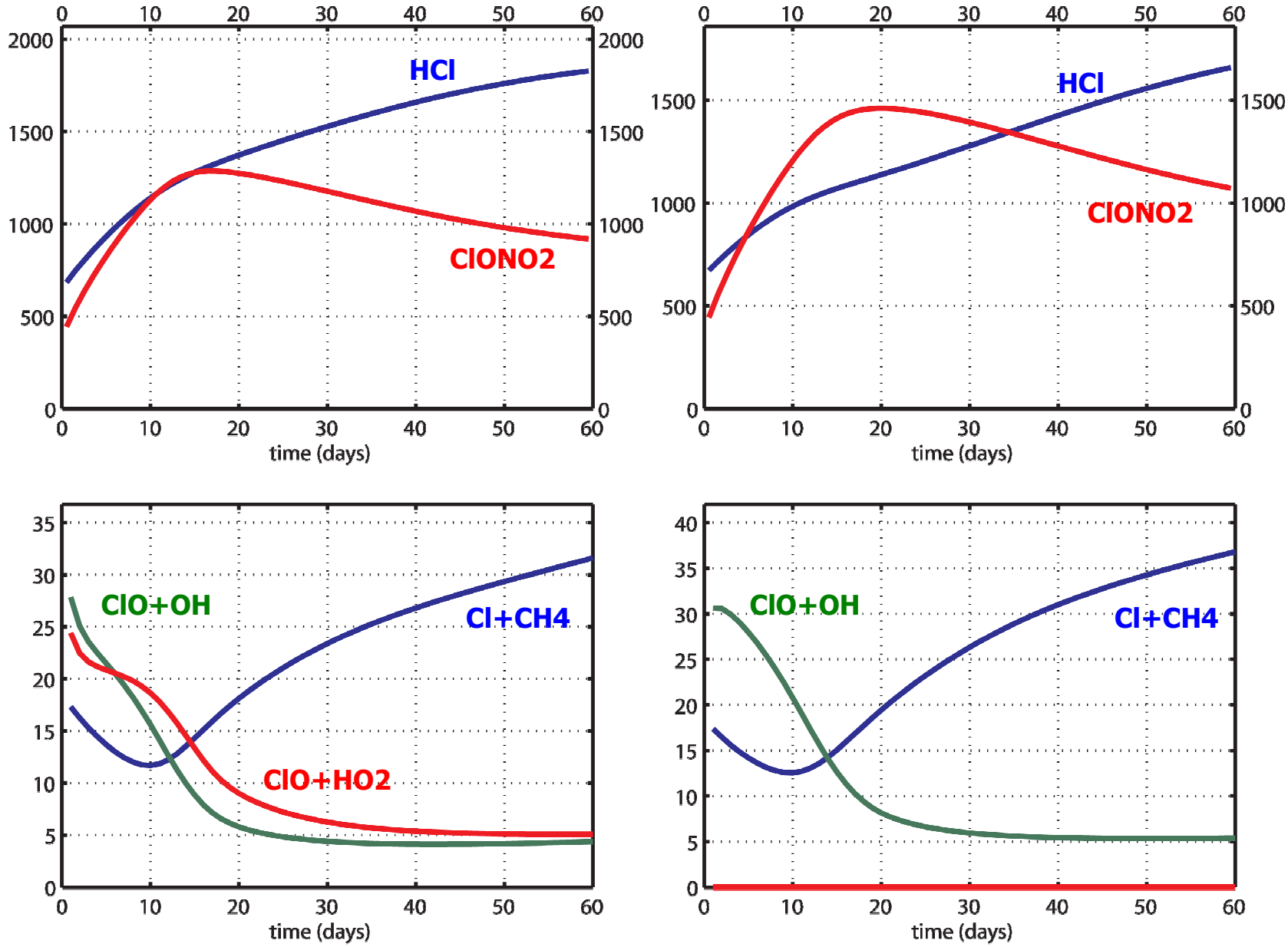
- Relative strengths of HCl and ClONO2 production rates are a function of O3 and HNO3.
- Reintroduction of NO2 from HNO3 photolysis and reaction with OH.
- Whenever NO2 production is occurring there will be appreciable HOx present.
- At least two HCl production paths and one ClONO2 production path.



Feb 15, 67 N, T=200 K, P=61 mb, initial Cly=Clx



Mar 1, 67 N, T=200K, P=61 mb, init 15% ClONO2, 25% HCl



Conclusions

HCl and ClONO2 gas-phase recovery rates can be are competitive.

The "1994" picture is incorrect.

The SOLVE ClOx and ClONO2 observations are consistent with the model predictions. The "low" ClONO2 observations indicate HCl must be of the same magnitude or higher.

ClONO2 recovery will be enhanced wrt HCl as HNO3 and O3 increase. Any additional HCl Prod mechanisms will enhance HCl recovery.

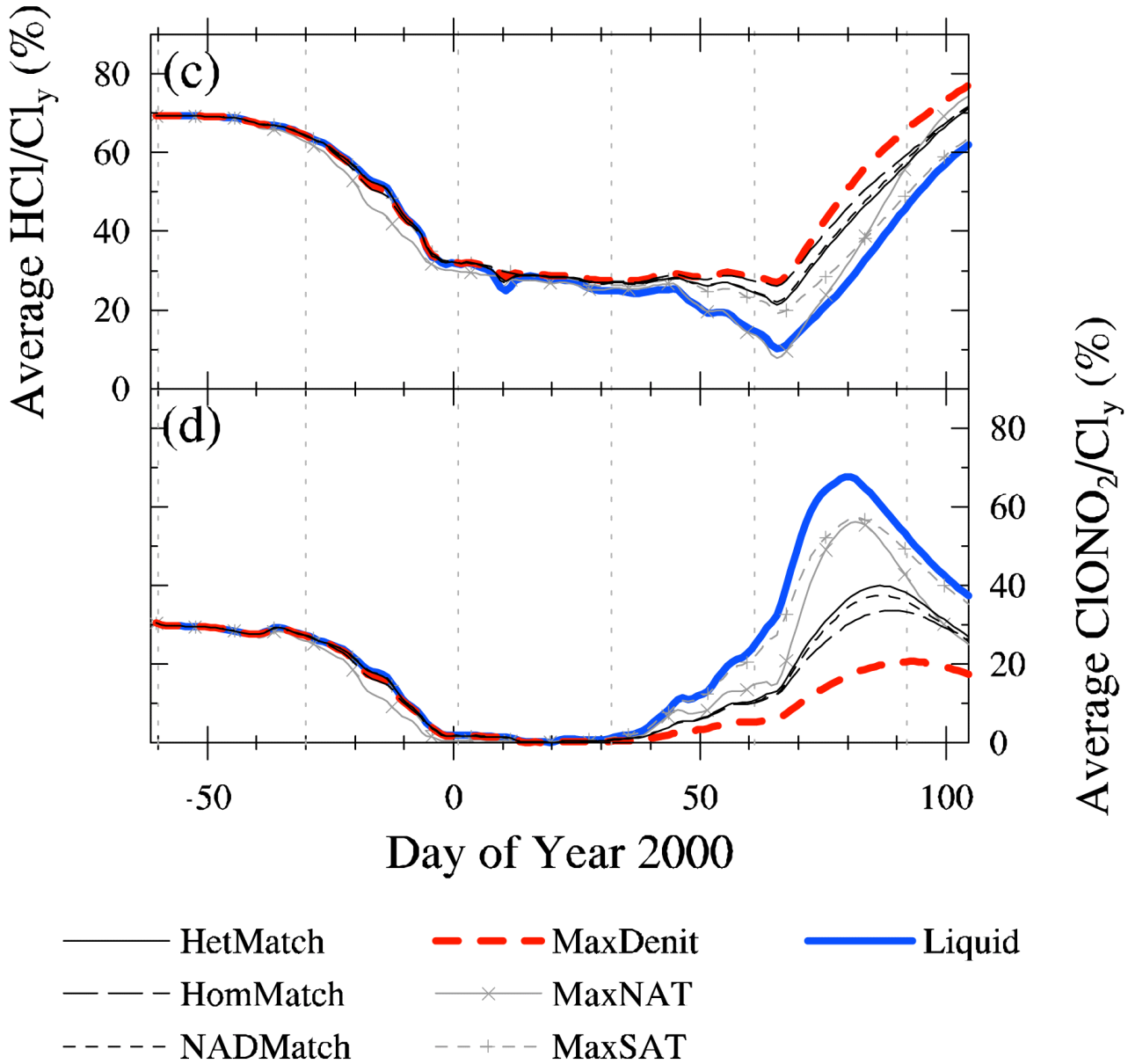
The HCl observations (ALIAS) are inconsistent with the ClONO2 observations and, from various other perspectives, do not "look good".

The Heterogeneous Reactions

$$ClONO_2 + HCl \xrightarrow{het} HNO3 + Cl_2$$

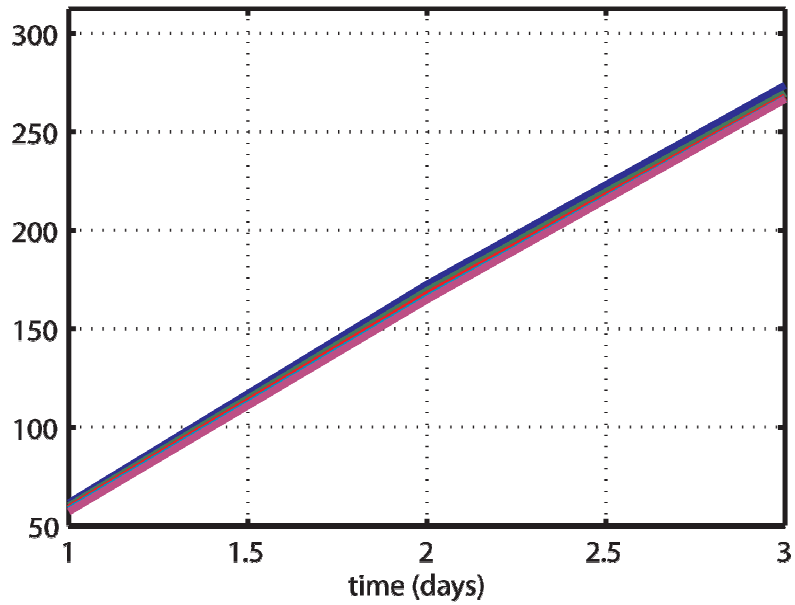
$$ClONO_2 + H_2O \xrightarrow{het} HOCl + HNO_3$$

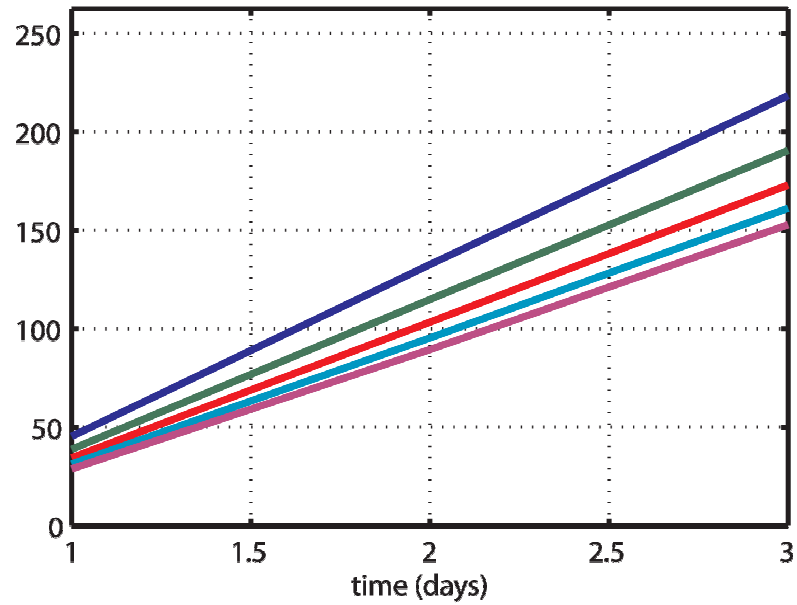
$$HOCl + HCl \xrightarrow{het} Cl_2 + H_2O$$

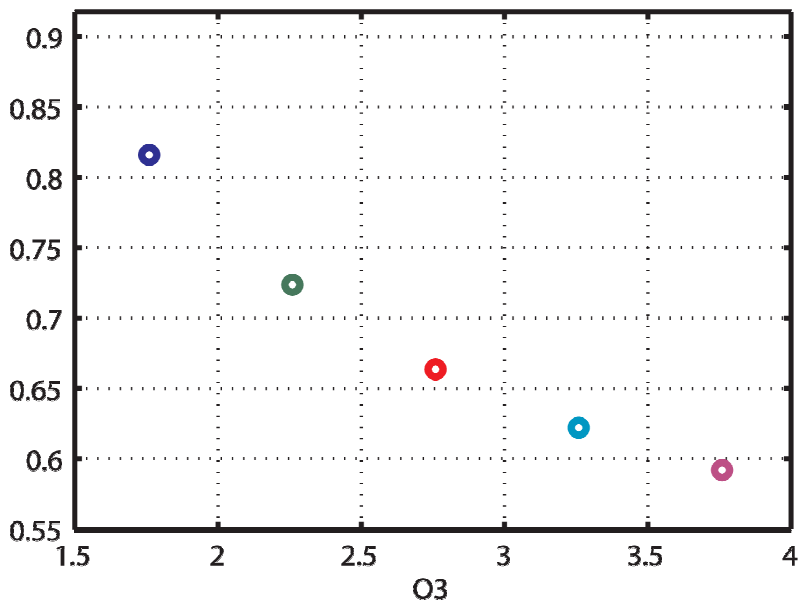


Adapted from Figure 5, Drdla and Schoeberl, JGR, 108, 8319 (2003)

O3 dependence







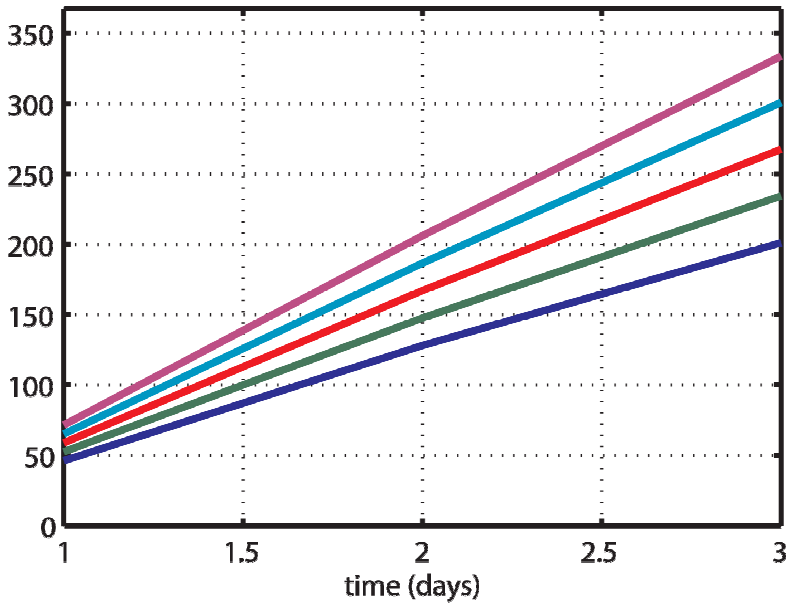
T = 200 K, P = 61 mbar, M = 2.21e+018
month = 3, Day = 1, Year = 2000
latitude = 67 N, longitude = 0

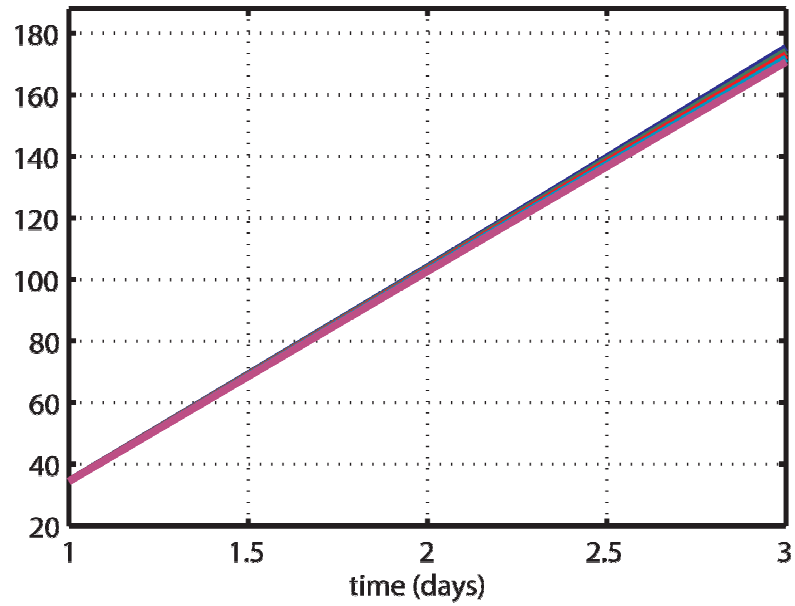
O3 loss rate, per day = 5.83 %
O3 start = 3.80 ppm, 8.39e+012 molec/cm3
O3 end = 3.58 ppm, 7.91e+012 molec/cm3
O3 net = 0.222 ppm, 4.90e+011 molec/cm3

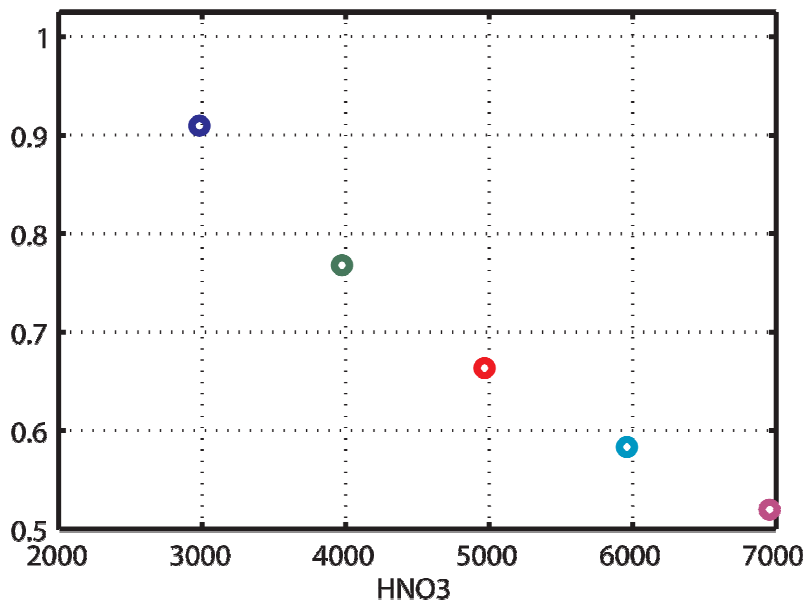
Cl = 0, ClO = 200, ClOOCl = 1150 ClONO2 = 0, HCl = 0
HOCl = 100 BrCl = 22 OClO = 200 Clx = 2500, Cly = 2822
Br = 0, BrO = 0, HOBr = 0 BrONO2 = 0
HBr = 0, BrCl = 22, Bry = 22
NO = 0, NO2 = 0, HNO3 = 5000 HNO4 = 100
NO3 = 0, N2O5 = 40, NOy = 5180
H2O = 5, CH4 = 1, H2 = 1 CH2O = 0

Run date = feb-01-05d, mat file = dumv10

HNO3 dependence







T = 200 K, P = 61 mbar, M = 2.21e+018
month = 3, Day = 1, Year = 2000
latitude = 67 N, longitude = 0

O3 loss rate, per day = 7.72 %
O3 start = 2.80 ppm, 6.19e+012 molec/cm3
O3 end = 2.58 ppm, 5.71e+012 molec/cm3
O3 net = 0.216 ppm, 4.77e+011 molec/cm3

Cl = 0, ClO = 200, ClOOCl = 1150 ClONO2 = 0, HCl = 0
HOCl = 100 BrCl = 22 OClO = 200 Clx = 2500, Cly = 2822
Br = 0, BrO = 0, HOBr = 0 BrONO2 = 0
HBr = 0, BrCl = 22, Bry = 22
NO = 0, NO2 = 0, HNO3 = 7000 HNO4 = 100
NO3 = 0, N2O5 = 40, NOy = 7180
H2O = 5, CH4 = 1, H2 = 1 CH2O = 0

Run date = feb-01-05d, mat file = dumv5